The Influence of Chemical Constitution upon Interfacial Tension.

By W. B. Hardy, F.R.S.

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If T_B be the pull per linear centimetre exerted by the surface tension of a pure fluid B, then, if the surface be increased by 1 sq. cm., the increase in surface energy is also T_B. Let a thin film of a second fluid A immiscible with B spread over the surface of B; the tension of the composite surface so formed is less than that of pure B, otherwise spreading would not occur. When the film of A has become sufficiently thick two independent surfaces are formed, one of pure A, the other the interface between A and B. Denoting these respectively by T_A and T_{AB} the energy of the two for each unit of the original surface of pure B is

$$T = T_A + T_{AB}, \tag{1}$$

and this quantity T is not affected by further addition of A. Therefore in the spreading of A upon B we have, as the limits of the change of surface energy, $T = B$ and $T = T_A + T_{AB}$.

In an earlier paper* I gave reasons for believing that the changes in the value of T between these limits depend mainly upon the chemical constitution of A.

Between the limits $T = T_B$ and $T = T_A + T_{AB}$, lies a series of values of T when A is not present in mass. The phenomena over this region are complex, therefore, in order to obtain a simpler presentation of the influence of chemical constitution it is necessary to have A as well as B present in mass. The equation then reduces to the simple form $T = T_{AB}$. It is with measurements of the quantity T_{AB} that we are concerned in this paper.

Following Dupré† we may write

$$T_{AB} = T_A + T_B - 2T'_{AB}, \tag{2}$$

in which $2T'_{AB}$ is the work done per unit of area of interface by the attraction of A for B when a surface of A is allowed to approach normally and touch a surface of B. Since the quantity $2T'_{AB}$ is the total work expended in forming unit area of interface by the molecular forces which operate between A and B it follows that evidence of the influence of chemical constitution upon surface energy must be looked for in a comparison of this quantity when different fluids A form an interface with a constant fluid B—

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* 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 610.

† 'Théorie Mécanique d. l. Chaleur,' Paris, 1869, p. 369. See also Lord Rayleigh, 'Phil. Mag.,' 1890, [5], vol. 30, p. 461.

in this case water. The tension T_{AB} will not serve our purpose so well since it depends directly upon the tension of A itself.

The first person to introduce the critical constants into considerations of surface energy was Eötvös,* and he was followed by Ramsay and Shields.† The argument may be stated as follows :—

In the gas equation $pv = R\theta$, if v be kept constant p decreases with fall of θ until where $p = 0$, $\theta = -273$ or absolute zero; the origin of the scale of temperature is thus also the origin of the scale of pressure. The absolute zero of surface energy is the critical temperature, and if an equation analogous to the gas equation be used, namely $Ta = K\tau$, in which a is the area of surface, the temperature τ must be measured in centigrade degrees downwards, the critical temperature being taken as zero. Corresponding to this equation the relation between tension and temperature should be a linear one—a relation proved experimentally by Ramsay and Shields. Near the critical point, however, the linear relation is departed from, with the result that the line which represents the relation between Ta and τ cuts the axis of temperature at a point some degrees below the critical point. The equation for the linear portion of the curve, that is for temperatures other than those near to the critical temperature, is therefore

$$Ta = K(\tau - d).$$

In comparing different substances that surface must be taken which is formed by the same number of molecules. Such a surface, as Eötvös pointed out, is the side of the cube which contains 1 gramme molecule. If v be the volume of a gramme molecule in cubic centimetres, that is the molecular volume, the area of the side of the cube will be $v^{2/3}$. Call this a molecular surface. The equation now becomes

$$Tv^{2/3} = K(\tau - d). \qquad (3)$$

This equation enables us to calculate the constant for the pure fluid A from measurements of T_A and T_{AB}.

Putting $(\tau - d) = 1$ in equation (3) we see that K is the gain in molecular surface energy per degree of temperature. An equation precisely similar to (3) for an interface would have as its zero of temperature, not the critical points of the pure fluids A and B, but the temperature at which A and B become completely miscible. This temperature is unknown for the pairs of substances used; an equation for the interface may, however, be derived from equations (2) and (3), namely

$$K_A = \frac{(T_{AB} + 2T'_{AB})\, v_A^{2/3} v_B^{2/3} - K_B(\tau_B - d)\, v_A^{2/3}.}{(\tau_A - d)\, v_B^{2/3}} \qquad (4)$$

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* 'Wied. Annal., vol. 27, p. 452.

† 'Phil. Trans.,' 1893, A, p. 647.

This equation enables us to calculate the constant for the pure fluid A from measurements of T_A and T_{AB}.

Experimental Methods.—These need somewhat detailed discussion. The surface tensions were measured by determining the weight of the drops of liquid delivered by certain capillary tubes, of which No. 1 was straight and No. 2 bent at right angles. The procedure may best be described by a random selection of an experiment.

Pure oleic acid was poured over some distilled water in a cylindrical vessel until it formed a layer about 3 cm. deep. The straight tube (No. 1), previously cleansed with sulphuric and chromic acids and washed out with distilled water, was dipped into the lower layer (distilled water) and enough fluid drawn up. The point of the tube being raised so as to be in the upper layer, the contents were allowed slowly to form drops which were counted while 3·56 c.c. of fluid left the tube. The operation was repeated with this result:—

Temperature, 20°. Tube 1. Capacity, 3·56 c.c.; number of drops, 44, 44·5, 43·8, 43·8.

Tube 2, bent at right angles, was next filled with the upper layer (oleic acid) and drops allowed to form and float up when the point was immersed in the lower layer (water).

Tube 2; capacity, 1·517 c.c. No. of drops, 37·1 : 37·2.

Tube 1 was then cleaned, dried, filled with oleic acid at 20° and a series of 10 drops allowed to fall into a weighed stoppered weighing bottle.

Weight of 10 drops, 0·1625, 0·1647, 0·1617, 0·1617. Mean, 0·1626.

Loss of weight by evaporation, determined by control experiment, 0·0000.

From these data we now have to calculate the quantities T_{AB} and T_A. The formula frequently used to compute the surface tension from the weight of a drop delivered by a tube is $T = mg/2\pi r$, when m is the weight of the drop and r the radius of the tube; but this formula gives little more than half the true surface tension. The weight of the drop cannot be calculated from statical consideration: the detachment of the drop is a dynamical effect. A complete solution of the dynamical problem is impracticable. It was attempted by Dupré* and the argument has been restated by Lord Rayleigh,† who found the formula $T = mg/3{\cdot}8r$ to be a close approximation for thin-walled tubes.

The tubes used by myself had the following dimensions at the orifice:—

No. 1. External radius, 0·1165 cm. Internal radius, 0·0615 cm.
No. 2. „ „ 0·0917 „ „ „ 0·0629 „

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* *Loc. cit.*, p. 327.

† 'Phil. Mag.,' 1899, [5], vol. 48, p. 321.

For these tubes the factor 3·8 was found too low. It applies apparently only to tubes of larger radius. This is at once seen when the tension of water is calculated from the weight of the drop delivered by tubes used by Lord Rayleigh.* The first six on his table give the following values:—

15°.		
r.	*m.*	T (factor 3·8).
cm.	grm.	
0·11175	0·0375	86·7
0·17017	0·0526	79·72
0·24256	0·0712	75·7
0·254	0·0755	76·7
0·32512	0·0923	73·2

For the smaller tubes therefore the tension comes out too high, the value for water at 15° being 74·45. I therefore determined experimentally the factor for water for tube 1 and found it 4·413 at 16° and 4·391 at 18·5°, and these values were used in computing my results. With Lord Rayleigh's values I now get for his smallest tube:—

15°. *r*, 0·11175; *m*, 0·0375; factor, 4·413; T, 74·64;

which agrees closely with the standard value 74·45.

For the quantity T_{AB} we have for the weight of the drop, if v be the volume of fluid delivered, n the number of drops and D_A the density of the upper layer, D_B that of the water: $m = v(D_B - D_A)g/n$ and the formula becomes

$$T_{AB} = \frac{v(D_B - D_A)g}{nrF}.$$

Returning to the actual experiment, when the lower layer forms drops in the upper layer since water wets the glass of the capillary tube they detach themselves from the whole face of the end of the tube, therefore r is here the external radius or $r = 0·1165$ cm. But when oleic acid is delivered into water by tube 2 it does not wet the walls and the drops are detached from the lumen, and r is the internal radius or 0·0629 cm. When oleic acid is delivered from tube 1 in air, however, it wets the walls and the external radius must be used.

We therefore have:—

$$\left.\begin{array}{llll} \text{Tube 1.} & \text{Mean number of drops, } 44, & r,\ 0·1165; & T_{AB},\ 15·66 \\ \text{Tube 2.} & \quad ,, \qquad\quad ,, \qquad 37·15 & r,\ 0·0629; & T_{AB},\ 14·64 \end{array}\right\}\text{Mean, } 15·15.$$

Tube 1. Weight of one drop of oleic acid in air, 0·1626; T_A, 31·15.

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* *Loc. cit.,* p. 324.

T_B, the tension of water at 20°, being 73·70, we get from equation (2)

$$T'_{AB} = 44{\cdot}85.$$

Inspection of Table III shows that the values of T_{AB} obtained for different substances with water sometimes agree closely for the two tubes, sometimes differ widely. How far may the means be trusted to give the true value? The best evidence that they do so is to be found in the consistent way in which the quantity T'_{AB} follows chemical constitution. The chief error arises from viscosity, for with very viscous fluids the drop takes an appreciable time to break away, therefore if the column of fluid in the capillary tube be moving with any velocity *at the time of breaking* the drop is over filled and the tension comes out too high. As an extreme case take the very viscid ricinolic acid at 16°, just above the temperature of solidification. When each drop occupied about 40 seconds in forming and breaking away the numbers were—Tube 1, 20·1, 20, 19·8. But when the time was reduced from 40 to 10 seconds the number fell to 8. Now with respect to this source of error the conditions are entirely dissimilar in the two tubes, in tube 1 a drop attached over the whole face is being filled by a stream of relatively small section, while in tube 2 the whole column of fluid which supports the drop is in movement. The concordance of the means leads one to conclude that in the first case the kinetic energy leads to over-inflation of a drop, while in the second case it causes the drop to break away too soon and therefore to be too small. Lord Rayleigh says that "sufficient time must be allowed for the normal formation of the drop," but the most important condition to observe is that the movement of the column of fluid in the tube should be as near as possible zero at the moment when the drop breaks away.

Where the critical constants are known the accuracy of the results may be tested by equations (3) and (4). Ramsay and Shields find that K = 2·21. I get the following, putting $d = 6$ as they do.

Table I.

	T_A.	$v^{2/3}$.	t°.	$(\tau - d)$.	K_A.
Carbon bisulphide	30·88	15·396	17	252	1·80
Carbon tetrachloride	24·51	20·999	17	260	1·98
Benzene	27·59	19·624	20·5	261·5	2·07
Toluene	26·82	22·154	22	292·5	2·03
Octylene	21·07	28·87	17·2	275·6	2·20
Cyclohexane	24·21	22·73	16·8	257	2·14
Ethyl-benzene	27·83	24·56	17·5	322·4	2·12
Octane	20·63	29·70	18·5	272	2·25

Rejecting the value for carbon bisulphide as being clearly too low, the order of agreement is the same as that found for various substances by Ramsay and Shields, and the mean is 2·11. Similarly from equation (4) we may calculate the constant K_A, using the interfacial tension T_{AB} as one of the data. The constant K_B, since the molecules of water associate in the fluid state to some multiple of the chemical molecule, is less than 2·11. The standard on which all measurements in this paper are based is $T_B = 74$ at 18°. Taking 365° as the critical temperature of water, equation (3) gives $K_B = 1·49$. Equation (4) now gives the following values for K_A:—

Table II.

Carbon bisulphide	1·88	Octylene	2·17
Carbon tetrachloride	1·98	Cyclohexane	2·16
Benzene	2·10	Ethylbenzene	2·12
Toluene	2·04	Octane	2·25

Here again the agreement justifies the conclusion that the mean value of T_{AB} is not far removed from the actual value. The most serious source of error, especially in the case of substances which have little power of lowering the tension of water, lies in the presence of more active impurities. Rigorous circumspection is necessary both in the handling of the water, and of the other fluids, and in their preparation. The effect of a trace of impurity is hardly to be credited. Cyclohexane, a saturated hydrocarbon, does not spread upon water. In some of it 0·00015 per cent. by weight of oleic acid was dissolved, making a 0·0004 normal solution. The fluid now flashed over a water surface and the tension of the interface with water was found to have fallen from 55·15, that of pure cyclohexane-water, to 32·37. It cannot be without interest to notice that the concentration of oleic acid employed is of the order of concentration needed in the case of such physiologically active substances as adrenalin reckoned as percentage of the body weight of the animal; also, if FitzGerald's view be true that the force of contraction of a muscle is derived from changes in the tension of internal surfaces, such a concentration of a similarly active body would reduce the absolute force by about 50 per cent. While dealing with the question of chemical purity certain special cases must be mentioned.

A sample of octane purchased from Kahlbaum gave the following values, T_{AB} 29·3, T'_{AB} 32·6. As these differed widely from the values obtained for other saturated bodies the sample was freed from unsaturated substances, by shaking for four weeks with many changes of concentrated sulphuric acid. It was then washed with water and distilled from metallic sodium, and the fraction which came over at 123—126° now gave the values

T_{AB} 53·48 and T'_{AB} 20·54, which accord with the values found for other saturated bodies.

Octylene, as obtained from Kahlbaum, gave T_{AB} 12·9, T'_{AB} 41. It was then distilled and a fraction of B.P. 122—124° collected, giving the values T_{AB} 22·48, T'_{AB} 36·24. Like octane it was found to be impossible to get a fraction giving a perfectly constant boiling point. A series of fractionations was therefore undertaken and two fractions collected, (A) 120—122°, (B) 122—124°, Bar. 758. The B.P. of octylene is given in Beilstem as 122—123°, and as 124·6° at 796·6 mm. Fraction A gave T_{AB} 22·61, T'_{AB} 36·18. Fraction B, T_{AB} 23·06, T'_{AB} 35·95.

The mean of these values is the best that can be got for octylene by fractional distillation.

The substances employed were for the most part purchased from Kahlbaum and, when possible, distilled to a constant boiling point just before use. Some specimens were lent to me by Dr. Ruhemann, to whom I owe also a great debt for his kindness in directly superintending and helping in the purification of each substance. Without the aid which his profound technical knowledge afforded I could not have succeeded in making the measurements.

The effect of any slight degree of mutual solubility of the fluids A and B upon the quantity T_{AB} needs consideration. Let T_a and T_b be respectively the tension of the saturated solution of B in A and of A in B which can form contiguous phases. We then have

$$T_{ab} = T_a + T_b - 2T'_{ab}. \tag{5}$$

Since $T_B > T_A$ in all the cases dealt with, $T_a > T_A$, and $T_b < T_B$, the relation of T'_{ab} to T'_{AB} so far as magnitude is concerned is uncertain, terms of opposite sign being introduced by the presence of A and B on both sides of the interface. When the two solutions are brought into contact the work done is derived from (1) the attraction of A for A and of B for B across the interface, and (2) the attraction of A for B. When pure A and B come into contact (1) is zero, and any degree of miscibility increases the work due to (1) and decreases that due to (2). Therefore, since mutual miscibility introduces effects of opposite signs into the right-hand members of equation (2), the relation of T_{ab} to T_{AB} cannot be predicted.* Whatever the theoretical conclusion practically the value of T_{AB} under the conditions of measurement was found to be sensibly independent of the state of the phases.

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* T_{ab} obviously does not include the loss of potential due to the mixing of A and B except at the interface, for, if it did, T_{ab} would be a function of the ratio surface/(mass of A + mass of B).

The alcohol cyclohexanol is soluble in 28 parts of water. Dry cyclohexanol on water gave the following values:—

16·2°. Density alcohol, 0·948, water = 1.

T_{AB}. Tube 1, 3·951; Tube 2, 3·665. Mean, 3·808.

The layers were then thoroughly shaken together in a stoppered vessel and left 24 hours. For the layers mutually saturated I got

16°. Density alcohol layer, 0·9538; density water layer, 0·9986.

T_{AB}. Tube 1, 3·912; Tube 2, 3·693. Mean, 3·802.

Benzene is slightly soluble in water. For two samples I found the following values. Benzene and water not shaken together T_{AB} (17°) 38·01, (20·5°) 36·84; mean 37·42; and after shaking together and leaving for 24 hours, T_{AB} (17°) 37·56, (20·5°) 37·58; mean 37·57.

The experimental results are gathered together in Table III. It will be noticed that whereas the interfacial tension (T_{AB}) only roughly follows the chemical constitution of the fluid A, the quantity T'_{AB} follows it very closely. That is to say, when unit area of a free surface of a fluid is brought into contact with unit area of the free surface of water, the loss of potential, or the work done by molecular forces, is determined by the chemical constitution of the former.

To illustrate this we have the first group of saturated substances, in which I have included oil "C," composed mainly of high boiling-point paraffins. T'_{AB} lies between 20·8 and 24. The introduction of an unsaturated linkage into the paraffin octane raises the value to 36 (octylene). But in the case of a ring compound unsaturated linkages produce a smaller effect, the number rising only to 32·26 (benzene).

The introduction of the OH group into a ring compound increases the quantity by 20 (cyclohexane and cyclohexanol, $51·43 - 21·63 = 19·8$); but the effect in the case of the paraffin chain is only about one-half. The presence of the carboxyl group produces the same effect as the OH group, the quantity being increased in the case of capryllic acid by 10·4.

For the esters we have 41 for ethyl hydrocinnamate. The introduction of one more unsaturated linkage increases this only slightly, namely, to the 43 of ethyl cinnamate, and the double ester ethyl phthalate again is only slightly higher, namely, 46. Other relations might be pointed out, but the figures speak for themselves. I prefer to pass on to the more important negative relations.

In the saturated bodies there is a very small but I believe real difference between the paraffin chain and the ring formation, and again between these and the compounds CS_2 and CCl_4. The two cyclic alcohols have practically

Table III.

Substance.	Boiling point.	Temp.	Density (D).	T_A.	T_B.	T_{AB}. I.	T_{AB}. II.	T_{AB}. Mean.	T'_{AB}.	v.	$v^{2/3}$.	$T'_{AB} \times v^{2/3}$.
Octane....................	123—126°	18°·5	0 ·7034	20 ·63	73 ·93	53 ·74	52 ·18	52 ·96	20 ·80	161 ·9	29 ·7	615
Cyclohexane	Abs. const.	16 ·8	0 ·779	24 ·21	74 ·2	56 ·00	54 ·31	55 ·15	21 ·63	108 ·4	22 ·73	492
Oil "C"	—	17 ·0	0 ·876	30 ·12	74 ·15	64 ·72	57 ·99	61 ·35	21 ·46	—	—	—
Carbon bisulphide	Abs. const.	16 ·0	1 ·253	30 ·88	74 ·3	58 ·15	54 ·15	56 ·15	24 ·51	60 ·42	15 ·396	377
Carbon tetrachloride ...	—	17 ·0	1 ·63	24 ·51	74 ·15	53 ·2	47 ·16	50 ·18	24 ·24	96 ·24	20 ·999	509
Octylene	122—124°	17 ·0	0 ·7255	20 ·82	74 ·15	22 ·91	22 ·07	22 ·48	36 ·24	155 ·18	28·87	1046
Benzene	Abs. const.	20 ·5	0 ·879	27 ·59	73 ·77	37 ·68	36 ·75	37 ·49	31 ·93	86·95	19 ·624	627
Toluene	Abs. const.	22 ·0	0 ·8646	26 ·5	73 ·40	37 ·35	34 ·70	36 ·02	31 ·94	104 ·3	22 ·154	708
p-Cymene	Abs. const.	13 ·5	0 ·8633	27 ·0	74 ·57	43 ·15	41 ·36	42 ·25	29 ·66	155 ·2	28 ·87	856
Styrene	144—148°	19 ·0	0 ·9028	30 ·54	73 ·85	39 ·70	38 ·20	38 ·95	32 ·72	114 ·5	23 ·58	771
Ethyl benzene	Abs. const.	17 ·5	0 ·879	27 ·83	74 ·07	33 ·93	32 ·90	33 ·41	34 ·24	121 ·56	24 ·56	841
Benzene iodide	Abs. const.	16 ·8	1 ·831	36 ·6	74 ·2	44 ·88	40 ·65	42 ·76	34 ·00	111 ·3	23 ·14	787
Ethyl iodide	Abs. const.	16 ·0	1 ·943	26 ·31	74 ·3	38 ·40	37 ·90	38 ·15	31 ·23	80 ·2	18 ·59	580
Capryllic acid (*n*)	Abs. const.	18 ·1	0 ·9116	27 ·3	74 ·0	8 ·43	8 ·35	8 ·39	46 ·45	157·9	29 ·21	1357
Oleic acid	Crystallises	20 ·0	0 ·898	30 ·99	73 ·70	15 ·73	14 ·71	15 ·22	44 ·73	314 ·0	46 ·19	2066
Ricinolic acid	(Kahlbaum)	16 ·0	0 ·9538	34 ·31	74 ·3	15 ·68	14 ·50	15 ·09	46 ·76	312 ·0	46 ·73	2185
Cyclohexanol	Abs. const.	16 ·2	0 ·9480	32 ·36	74 ·3	3 ·951	3 ·665	3 ·808	51 ·43	105 ·5	23 ·77	1223
Octyl alcohol	Abs. const.	17 ·5	0 ·8293	26 ·19	74 ·07	8 ·053	7 ·882	7 ·967	46 ·14	156 ·6	29 ·04	1340
Benzyl alcohol	Abs. const.	22 ·5	1 ·0442	37 ·93	73 ·33	4 ·898	4 ·891	4 ·894	53 ·18	101 ·6	21 ·77	1158
Ethyl phthalate.........	Abs. const.	20 ·5	1 ·1175	35 ·26	73 ·48	17 ·10	17 ·06	17 ·08	45 ·83	—	—	—
Ethyl cinnamate	Abs. const.	19 ·5	1 ·0497	36 ·59	73 ·63	24 ·01	24 ·48	24 ·24	43 ·00	167 ·7	30 ·41	1308
Ethyl hydrocinnamate	Abs. const.	21 ·5	1 ·014	33·23	73 ·48	24 ·30	24 ·73	24 ·5	41 ·02	175 ·2	31 ·31	1284
Castor oil	—	17 ·0	0 ·966	35 ·27	74 ·15	26 ·2	19 ·7	23 ·0	43 ·26	—	—	—

v is the volume of one gramme molecule, $v^{2/3}$ the molecular surface.

the same value, and the three fatty acids agree closely. Similarly benzene and the allied substances give values close together. But the remarkable feature of these correspondences is that they are for unit area of interface and not for areas on which equal numbers of molecules impinge.

In the gas equation $Pv = R\theta$ the constant R refers to a volume which contains 1 gramme molecule. Similarly, in the comparison of surface energy, as Eötvös showed (*loc. cit.*), surfaces of the same molecular value must be compared. Such a molecular surface is the face of a cube which holds a gramme molecule of the fluid—or $v^{2/3}$. Tables I and II prove that the values found for T_A and T_{AB} are consistent with this conception of equi-molecular surfaces. But the values for T'_{AB}, though derived from T_A and T_{AB}, are in respect to their relation to chemical constitution independent of the area of the molecular surface. To put the matter in another way—agreement in the values for a particular type of substance, say, saturated compounds, or acids, would by analogy be between the product of the quantities T'_{AB}, which refers to unit area, and the molecular surface ($v^{2/3}$). The last column in Table III shows that this product follows no regular system.

This remarkable fact may be interpreted in various ways, but from whatever aspect it is considered the result is likely to be barren unless molecules are taken account of. If the figures in Table III are interpreted to mean that the energy peculiar to an interface between two fluids is determined by the chemical reaction between the fluids, we may conclude that such action will be complete and independent of the molecular volumes, since the mass of the fluids on either side of the interface is practically infinite. Against this view, however, it is to be noted that chemical action between water and such stable substances as paraffin or cyclohexane, both in mass, is unknown. If it did occur at an interface it could only be as the result of great stresses.

Table III shows most clearly that the quantity T'_{AB} increases with what may be called the chemical reactivity of the fluid B, and especially that it is greatest when the molecules are of the salt type—acids, alcohols, or esters. Such molecules by their constitution readily exhibit electric polarisation, and we have here additional evidence for the fact mentioned in the earlier papers that the chief modifying factor in all interfaces is the development of a contact difference of potential, due to polarisation of the molecules by stresses normal to the interface. If the quantity T'_{AB} represents mainly the specific electric polarisation of the interface, then its value for paraffin, cyclohexane, etc., may represent polarisation due to the water molecules, which are of this salt type. For a surface between two saturated substances not of salt type the quantity might well be zero, in which case we should have

$$T_{AB} = T_A + T_B.$$

From the fact that T'_{AB} is equal for molecules of the same chemical type two conclusions follow. Let each molecule of A attract a molecule of B by a force which is a function only of the distance which separates them, the density term in the Laplacian theory then becomes the reciprocal of the molecular volume and, following the usual notation,

$$T'_{AB} = \frac{\pi}{v_A v_B}\int_0^\infty z\psi_{AB}(z)\,dz,$$

v_A, v_B, being respectively the molecular volumes, and z the axis normal to the interface. Then on Young's hypothesis, that molecular attraction is a force which is of constant value over the range a, we have for two similar chemical substances, for which therefore T'_{AB} is the same, $a_1/a_2 = v_A'/v_A''$ That is to say, the range would be proportional to the molecular volume.

The alternative assumption, that the attractive force of a molecule of A for one of B falls off according to some power of the distance which separates them, yields the result that for similar chemical substances, since T'_{AB} is equal, the molecular volumes vary inversely with this power. Thus, if the attractive force $\phi(f)$ be put $= e^{-\beta f}$ then $v_A'/v_A'' = \beta_{,,}^5/\beta_{,}^5$.

The Tension of Composite Fluid Surfaces.—No. II.

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With the figures in Table III of the preceding paper (p. 311) as a guide the problem of the spreading of one fluid over the surface of another may be approached with some sense of security. In an earlier paper* the equation of a composite surface was found to be $T_S = T_A + T_{AB} - Kg$ when T_S is the tension of the composite surface, and Kg a term depending upon gravity. Putting $Kg = 0$, it is seen that spreading will occur only when $T_S > T_A + T_{AB}$, and, at the limit, $T_S = T_B$ that is to the tension of pure water in the experiments under consideration.

Taking $T_B = 74$, the tension of pure water, we have from the last paper

Table I.

	T_A.		T_{AB}.		
Cyclohexane	24·21	+	55·15	=	79·36
Octane	20·63		52·96		73·59
Oil "C"	30·12		61·35		91·47
Carbon disulphide	30·88		56·15		87·03
Carbon tetrachloride	24·51		50·18		74·69

* 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 610.